

# Methyl 2,6-bis[(5-chloro-4,6-dimethoxy-pyrimidin-2-yl)oxy]benzoate

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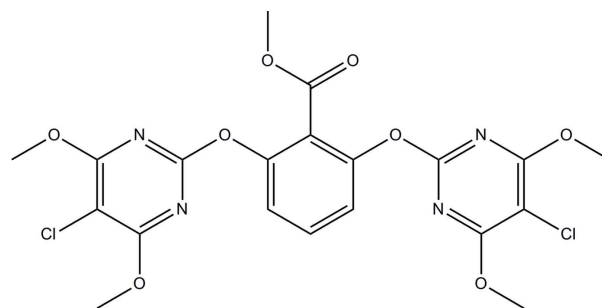
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.129; data-to-parameter ratio = 25.8.

In the title compound,  $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_8$ , the two pyrimidine rings are inclined at dihedral angles of 66.68 (5) and 71.91 (6)° with respect to the central benzene ring. In the crystal structure, intermolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bonds link neighbouring molecules into a ribbon-like structure along the  $b$  axis. The ribbons are interconnected into a two-dimensional network parallel to the  $bc$  plane by short intermolecular  $\text{Cl}\cdots\text{Cl}$  [3.4427 (6) Å] and  $\text{Cl}\cdots\text{O}$  [3.1420 (9) and 3.1750 (11) Å] interactions. The crystal structure is further stabilized by intermolecular  $\pi-\pi$  interactions [centroid-centroid distance 3.4552 (8) Å] involving the pyrimidine rings.

## Related literature

For general background to and applications of the title compound, see: Koichiro *et al.* (1988, 1998); He *et al.* (2007); Li *et al.* (2006); Geroge (1983). For graph-set descriptions of hydrogen-bonded ring motifs, see: Bernstein *et al.* (1995). For a closely related structure, see: Li & Luo (2006). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



## Experimental

### Crystal data

$\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_8$   $V = 4475.7$  (7) Å<sup>3</sup>  
 $M_r = 513.28$   $Z = 8$   
 Monoclinic,  $C2/c$   $\text{Mo } K\alpha$  radiation  
 $a = 29.354$  (3) Å  $\mu = 0.35$  mm<sup>-1</sup>  
 $b = 8.0485$  (8) Å  $T = 100$  K  
 $c = 22.5923$  (19) Å  $0.58 \times 0.31 \times 0.16$  mm  
 $\beta = 123.014$  (2)°

### Data collection

Bruker APEXII DUO CCD area-detector diffractometer 22170 measured reflections  
 8040 independent reflections  
 Absorption correction: multi-scan (SADABS; Bruker, 2009) 6824 reflections with  $I > 2\sigma(I)$   
 $T_{\min} = 0.825$ ,  $T_{\max} = 0.948$   $R_{\text{int}} = 0.023$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$  312 parameters  
 $wR(F^2) = 0.129$  H-atom parameters constrained  
 $S = 1.08$   $\Delta\rho_{\max} = 0.71$  e Å<sup>-3</sup>  
 8040 reflections  $\Delta\rho_{\min} = -0.55$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C16}-\text{H16A}\cdots\text{N1}^i$	0.96	2.58	3.5018 (19)	161
$\text{C20}-\text{H20A}\cdots\text{N3}^{ii}$	0.96	2.59	3.5148 (19)	161

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x, y+1, z$ .

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2009).

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§ Thomson Reuters ResearcherID: C-7576-2009.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5115).

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**supplementary materials**

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## Methyl 2,6-bis[(5-chloro-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

H.-K. Fun, J. H. Goh, S. Rai, A. M. Isloor and P. Shetty

### Comment

Methyl-2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate is a derivative of herbicide showing excellent herbicidal effects on annual and perennial weeds and high-safety crops, especially rice and wheat and is applied to paddy fields, ploughed fields and non-agricultural land (Koichiro *et al.*, 1988, 1998). Most sulphonylurea herbicides and all pyrimidinylbenzoate herbicides (He *et al.*, 2007) such as nicofulfuron, amidosulfuron, halopyrazosulfuron, ethoxysulfuron, pyriminobac-methyl and pyrifthalid, possess 4,6-dimethoxypyrimidin-2-yl groups (Li *et al.*, 2006), while sulfometuron-methyl, a kind of sulphonylurea, contains 4,6-dimethylpyrimidin-2-yl groups, which suggests that the two disubstituted pyrimidin-2-yl groups possess high biological activity (Gerorge, 1983).

In the title compound (Fig. 1), the two pyrimidine rings (C1-C4/N1/N2 and C11-C14/N3/N4) are essentially planar, with maximum deviations of 0.011 (1) and 0.007 (1) Å, respectively, at atoms N1 and N4. The central phenyl ring is inclined at dihedral angles of 66.68 (5) and 71.91 (6)°, respectively, with respect to the C1-C4/N1/N2 and C11-C14/N3/N4 pyrimidine rings. The bond lengths and angles are consistent with a closely related structure (Li & Luo, 2006).

In the crystal structure, intermolecular C16—H16A···N1 and C20—H20A···N3 hydrogen bonds (Table 1) link neighbouring molecules into a ribbon-like structure containing  $R^2_2(26)$  ring motifs (Fig. 2, Bernstein *et al.*, 1995), along the *b* axis. The interesting features of the crystal structure are the intermolecular short Cl···Cl [C11···Cl2<sup>iii</sup> = 3.4427 (6) Å; (iii) 1/2-*x*2, *y*-1/2, 1/2-*z*] and Cl···O [C11···O8<sup>iii</sup> = 3.1750 (11) and Cl2···O1<sup>iv</sup> = 3.1420 (9) Å; (iv) *x*, 2-*y*, *z*+1/2] interactions, which are shorter than the sum of the van der Waals radii of the relevant atoms, interconnecting the ribbons into two-dimensional networks parallel to the *bc* plane. The crystal structure is further stabilized by weak intermolecular  $\pi$ - $\pi$  interactions [Cg1···Cg1<sup>v</sup> = 3.4552 (8) Å; (v) -*x*, *y*, -*z*+1/2; Cg1 is the centroid of C11-C14/N3/N4 pyrimidine ring].

### Experimental

To a stirred solution of methyl-2,6-dihydroxybenzoate (0.50 g, 0.0026 mol) in acetonitrile (10 ml) was added potassium carbonate (1.00 g, 0.0070 mol) and 5-chloro-4,6-dimethoxy-2-(methylsulfonyl)pyrimidine (1.58 g, 0.0050 mol). The reaction mixture was heated to reflux for 4 h. Mass analysis showed completion of the reaction. The reaction mixture was filtered and the filtrate was concentrated. The residue was recrystallized using dichloromethane to obtain the title compound (yield: 67 %, m.p. 427–430 K).

### Refinement

All H atoms were placed in the calculated positions, with C—H = 0.93–0.96 Å, and refined using a riding model with  $U_{iso} = 1.2$  or  $1.5 U_{eq}(C)$ . The rotating group model was used for the methyl groups.

## Figures

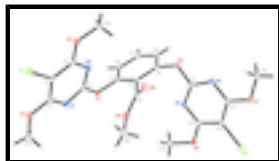


Fig. 1. The molecular structure of the title compound, showing 30 % probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

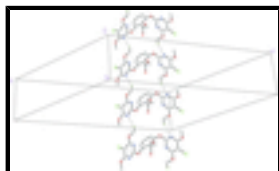


Fig. 2. Part of the crystal structure, viewed along an arbitrary axis, showing a molecular ribbon. H atoms not involved in hydrogen bonds (dashed lines) have been omitted for clarity.

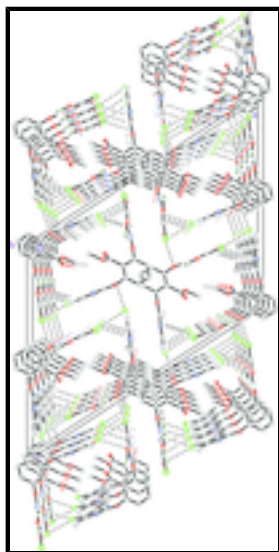


Fig. 3. The crystal structure of the title compound, viewed along the *b* axis, showing two-dimensional networks parallel to the *bc* plane. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

## Methyl 2,6-bis[(5-chloro-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

### Crystal data

$C_{20}H_{18}Cl_2N_4O_8$

$M_r = 513.28$

Monoclinic,  $C2/c$

Hall symbol:  $-C 2yc$

$a = 29.354 (3) \text{ \AA}$

$b = 8.0485 (8) \text{ \AA}$

$c = 22.5923 (19) \text{ \AA}$

$\beta = 123.014 (2)^\circ$

$V = 4475.7 (7) \text{ \AA}^3$

$Z = 8$

$F(000) = 2112$

$D_x = 1.523 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 9948 reflections

$\theta = 2.7\text{--}32.6^\circ$

$\mu = 0.35 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, colourless

$0.58 \times 0.31 \times 0.16 \text{ mm}$

### Data collection

Bruker APEXII DUO CCD area-detector

8040 independent reflections

diffractometer	
Radiation source: fine-focus sealed tube	6824 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.023$
$\varphi$ and $\omega$ scans	$\theta_{\text{max}} = 32.6^\circ$ , $\theta_{\text{min}} = 1.7^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$h = -44 \rightarrow 43$
$T_{\text{min}} = 0.825$ , $T_{\text{max}} = 0.948$	$k = -12 \rightarrow 12$
22170 measured reflections	$l = -34 \rightarrow 34$

### Refinement

Refinement on $F^2$	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 1.9869P]$
8040 reflections	where $P = (F_o^2 + 2F_c^2)/3$
312 parameters	$(\Delta/\sigma)_{\text{max}} = 0.001$
0 restraints	$\Delta\rho_{\text{max}} = 0.71 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.55 \text{ e } \text{\AA}^{-3}$

### Special details

**Experimental.** The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional R-factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and R-factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.307309 (11)	0.57598 (4)	0.096234 (18)	0.02454 (8)
C12	0.082300 (12)	0.91419 (4)	0.399331 (14)	0.01982 (8)
O1	0.11797 (3)	0.91625 (11)	0.04367 (4)	0.01529 (16)
O2	0.04987 (3)	0.57525 (11)	0.15715 (4)	0.01615 (16)
O3	0.28912 (4)	0.93539 (12)	0.08837 (5)	0.02288 (19)
O4	0.20796 (3)	0.42435 (11)	0.07368 (5)	0.01987 (17)
O5	0.16660 (4)	0.88991 (14)	0.18631 (5)	0.0263 (2)
O6	0.16179 (4)	0.62171 (15)	0.20959 (5)	0.0296 (2)

## supplementary materials

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O7	0.07442 (4)	0.55550 (12)	0.37357 (4)	0.01848 (17)
O8	0.07019 (4)	1.06655 (11)	0.27317 (4)	0.01907 (17)
N1	0.20277 (4)	0.92889 (13)	0.06785 (5)	0.01634 (18)
N2	0.16079 (4)	0.66706 (13)	0.05757 (5)	0.01477 (17)
N3	0.06228 (4)	0.56256 (13)	0.26376 (5)	0.01535 (18)
N4	0.06122 (4)	0.82430 (13)	0.21320 (5)	0.01471 (17)
C1	0.24667 (4)	0.84915 (16)	0.07879 (6)	0.0167 (2)
C2	0.25047 (4)	0.67647 (16)	0.08112 (6)	0.0171 (2)
C3	0.20559 (4)	0.58939 (15)	0.07043 (5)	0.0152 (2)
C4	0.16281 (4)	0.83107 (15)	0.05732 (5)	0.01390 (19)
C5	0.07753 (4)	0.82779 (14)	0.04464 (5)	0.01343 (18)
C6	0.02637 (4)	0.83115 (16)	-0.01690 (5)	0.0172 (2)
H6A	0.0207	0.8867	-0.0565	0.021*
C7	-0.01650 (4)	0.75105 (17)	-0.01925 (6)	0.0206 (2)
H7A	-0.0510	0.7533	-0.0605	0.025*
C8	-0.00804 (4)	0.66766 (16)	0.03972 (6)	0.0179 (2)
H8A	-0.0366	0.6133	0.0382	0.022*
C9	0.04341 (4)	0.66658 (15)	0.10068 (5)	0.01393 (18)
C10	0.08739 (4)	0.74658 (14)	0.10524 (5)	0.01335 (18)
C11	0.05844 (4)	0.66055 (15)	0.21417 (5)	0.01376 (18)
C12	0.06937 (4)	0.64190 (16)	0.32011 (5)	0.01463 (19)
C13	0.07199 (4)	0.81463 (15)	0.32568 (5)	0.01496 (19)
C14	0.06775 (4)	0.90169 (15)	0.26965 (5)	0.01476 (19)
C15	0.28520 (6)	1.11370 (19)	0.08786 (9)	0.0296 (3)
H15A	0.3151	1.1619	0.0877	0.044*
H15B	0.2863	1.1497	0.1291	0.044*
H15C	0.2516	1.1484	0.0464	0.044*
C16	0.16177 (5)	0.33858 (18)	0.06581 (8)	0.0262 (3)
H16A	0.1695	0.2218	0.0735	0.039*
H16B	0.1306	0.3562	0.0190	0.039*
H16C	0.1545	0.3807	0.0997	0.039*
C17	0.14212 (4)	0.74193 (17)	0.17246 (6)	0.0187 (2)
C18	0.22073 (7)	0.8981 (3)	0.24900 (9)	0.0473 (5)
H18A	0.2353	1.0076	0.2534	0.071*
H18B	0.2435	0.8182	0.2456	0.071*
H18C	0.2194	0.8740	0.2897	0.071*
C19	0.07186 (6)	0.37652 (18)	0.36714 (6)	0.0226 (2)
H19A	0.0735	0.3285	0.4072	0.034*
H19B	0.1019	0.3373	0.3653	0.034*
H19C	0.0384	0.3449	0.3247	0.034*
C20	0.07386 (7)	1.15252 (18)	0.21994 (7)	0.0286 (3)
H20A	0.0771	1.2698	0.2292	0.043*
H20B	0.0418	1.1311	0.1743	0.043*
H20C	0.1052	1.1140	0.2209	0.043*

Atomic displacement parameters ( $\text{\AA}^2$ )

$U^{11}$

$U^{22}$

$U^{33}$

$U^{12}$

$U^{13}$

$U^{23}$

Cl1	0.01660 (12)	0.02313 (16)	0.03475 (16)	0.00517 (10)	0.01454 (11)	0.00213 (12)
Cl2	0.02636 (14)	0.02056 (15)	0.01647 (12)	−0.00313 (10)	0.01420 (10)	−0.00502 (9)
O1	0.0144 (3)	0.0143 (4)	0.0208 (3)	0.0030 (3)	0.0119 (3)	0.0037 (3)
O2	0.0246 (4)	0.0139 (4)	0.0150 (3)	−0.0023 (3)	0.0141 (3)	−0.0023 (3)
O3	0.0179 (4)	0.0186 (4)	0.0352 (5)	0.0000 (3)	0.0164 (3)	0.0014 (4)
O4	0.0170 (3)	0.0131 (4)	0.0280 (4)	0.0012 (3)	0.0113 (3)	−0.0011 (3)
O5	0.0220 (4)	0.0305 (5)	0.0185 (4)	−0.0102 (4)	0.0060 (3)	−0.0027 (4)
O6	0.0222 (4)	0.0338 (6)	0.0234 (4)	0.0043 (4)	0.0064 (3)	0.0104 (4)
O7	0.0266 (4)	0.0176 (4)	0.0158 (3)	−0.0012 (3)	0.0144 (3)	0.0008 (3)
O8	0.0267 (4)	0.0131 (4)	0.0175 (3)	0.0004 (3)	0.0121 (3)	−0.0015 (3)
N1	0.0160 (4)	0.0151 (5)	0.0205 (4)	0.0010 (3)	0.0116 (3)	0.0012 (3)
N2	0.0148 (4)	0.0142 (4)	0.0162 (3)	0.0020 (3)	0.0090 (3)	0.0003 (3)
N3	0.0185 (4)	0.0154 (5)	0.0155 (4)	−0.0007 (3)	0.0114 (3)	−0.0009 (3)
N4	0.0179 (4)	0.0139 (4)	0.0139 (3)	0.0006 (3)	0.0097 (3)	−0.0008 (3)
C1	0.0146 (4)	0.0176 (5)	0.0190 (4)	−0.0001 (4)	0.0100 (3)	0.0005 (4)
C2	0.0141 (4)	0.0174 (5)	0.0206 (4)	0.0033 (4)	0.0100 (3)	0.0008 (4)
C3	0.0153 (4)	0.0142 (5)	0.0156 (4)	0.0023 (4)	0.0081 (3)	0.0002 (4)
C4	0.0135 (4)	0.0156 (5)	0.0140 (4)	0.0023 (4)	0.0083 (3)	0.0011 (4)
C5	0.0142 (4)	0.0135 (5)	0.0155 (4)	0.0013 (4)	0.0100 (3)	−0.0001 (4)
C6	0.0165 (4)	0.0212 (6)	0.0144 (4)	0.0016 (4)	0.0088 (3)	0.0019 (4)
C7	0.0154 (4)	0.0270 (7)	0.0167 (4)	−0.0003 (4)	0.0071 (3)	0.0010 (4)
C8	0.0162 (4)	0.0211 (6)	0.0182 (4)	−0.0024 (4)	0.0105 (4)	−0.0020 (4)
C9	0.0178 (4)	0.0133 (5)	0.0137 (4)	−0.0001 (4)	0.0105 (3)	−0.0011 (4)
C10	0.0144 (4)	0.0136 (5)	0.0130 (4)	0.0007 (3)	0.0081 (3)	−0.0009 (3)
C11	0.0146 (4)	0.0154 (5)	0.0136 (4)	−0.0007 (4)	0.0092 (3)	−0.0020 (4)
C12	0.0146 (4)	0.0177 (5)	0.0135 (4)	−0.0005 (4)	0.0089 (3)	0.0000 (4)
C13	0.0171 (4)	0.0161 (5)	0.0139 (4)	−0.0004 (4)	0.0099 (3)	−0.0025 (4)
C14	0.0153 (4)	0.0142 (5)	0.0149 (4)	0.0006 (4)	0.0083 (3)	−0.0013 (4)
C15	0.0243 (6)	0.0186 (6)	0.0490 (8)	−0.0024 (5)	0.0220 (6)	0.0008 (6)
C16	0.0207 (5)	0.0153 (6)	0.0407 (7)	−0.0013 (4)	0.0155 (5)	−0.0015 (5)
C17	0.0161 (4)	0.0242 (6)	0.0156 (4)	−0.0012 (4)	0.0085 (3)	0.0002 (4)
C18	0.0290 (7)	0.0602 (13)	0.0281 (7)	−0.0201 (8)	−0.0003 (6)	−0.0017 (7)
C19	0.0323 (6)	0.0183 (6)	0.0214 (5)	−0.0017 (5)	0.0173 (4)	0.0016 (5)
C20	0.0497 (8)	0.0162 (6)	0.0220 (5)	0.0018 (6)	0.0209 (5)	0.0020 (5)

*Geometric parameters (Å, °)*

Cl1—C2	1.7126 (11)	C5—C6	1.3834 (14)
Cl2—C13	1.7187 (11)	C5—C10	1.3978 (14)
O1—C4	1.3621 (12)	C6—C7	1.3889 (16)
O1—C5	1.3944 (13)	C6—H6A	0.93
O2—C11	1.3569 (12)	C7—C8	1.3881 (16)
O2—C9	1.3929 (13)	C7—H7A	0.93
O3—C1	1.3370 (14)	C8—C9	1.3824 (14)
O3—C15	1.4393 (18)	C8—H8A	0.93
O4—C3	1.3301 (14)	C9—C10	1.3952 (14)
O4—C16	1.4436 (15)	C10—C17	1.4934 (15)
O5—C17	1.3370 (16)	C12—C13	1.3943 (17)
O5—C18	1.4432 (17)	C13—C14	1.3918 (15)



## supplementary materials

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O6—C17	1.2023 (16)	C15—H15A	0.96
O7—C12	1.3301 (13)	C15—H15B	0.96
O7—C19	1.4457 (16)	C15—H15C	0.96
O8—C14	1.3288 (14)	C16—H16A	0.96
O8—C20	1.4415 (15)	C16—H16B	0.96
N1—C4	1.3224 (14)	C16—H16C	0.96
N1—C1	1.3365 (14)	C18—H18A	0.96
N2—C4	1.3215 (16)	C18—H18B	0.96
N2—C3	1.3372 (14)	C18—H18C	0.96
N3—C11	1.3238 (14)	C19—H19A	0.96
N3—C12	1.3353 (13)	C19—H19B	0.96
N4—C11	1.3214 (16)	C19—H19C	0.96
N4—C14	1.3360 (13)	C20—H20A	0.96
C1—C2	1.3930 (18)	C20—H20B	0.96
C2—C3	1.3923 (15)	C20—H20C	0.96
C4—O1—C5	117.72 (9)	N3—C11—O2	112.86 (10)
C11—O2—C9	117.70 (9)	O7—C12—N3	119.87 (11)
C1—O3—C15	116.92 (10)	O7—C12—C13	117.78 (9)
C3—O4—C16	116.97 (9)	N3—C12—C13	122.35 (10)
C17—O5—C18	115.74 (13)	C14—C13—C12	116.54 (9)
C12—O7—C19	117.10 (9)	C14—C13—Cl2	121.81 (9)
C14—O8—C20	117.10 (9)	C12—C13—Cl2	121.61 (8)
C4—N1—C1	114.76 (11)	O8—C14—N4	119.85 (10)
C4—N2—C3	115.27 (9)	O8—C14—C13	118.24 (10)
C11—N3—C12	114.78 (10)	N4—C14—C13	121.92 (11)
C11—N4—C14	115.29 (9)	O3—C15—H15A	109.5
N1—C1—O3	120.02 (11)	O3—C15—H15B	109.5
N1—C1—C2	122.37 (10)	H15A—C15—H15B	109.5
O3—C1—C2	117.60 (10)	O3—C15—H15C	109.5
C3—C2—C1	116.54 (10)	H15A—C15—H15C	109.5
C3—C2—C11	121.59 (10)	H15B—C15—H15C	109.5
C1—C2—C11	121.87 (9)	O4—C16—H16A	109.5
O4—C3—N2	119.63 (10)	O4—C16—H16B	109.5
O4—C3—C2	118.50 (10)	H16A—C16—H16B	109.5
N2—C3—C2	121.87 (11)	O4—C16—H16C	109.5
N2—C4—N1	129.15 (10)	H16A—C16—H16C	109.5
N2—C4—O1	117.63 (9)	H16B—C16—H16C	109.5
N1—C4—O1	113.22 (10)	O6—C17—O5	124.13 (11)
C6—C5—O1	116.19 (9)	O6—C17—C10	124.84 (12)
C6—C5—C10	121.70 (9)	O5—C17—C10	111.03 (10)
O1—C5—C10	122.04 (9)	O5—C18—H18A	109.5
C5—C6—C7	119.62 (10)	O5—C18—H18B	109.5
C5—C6—H6A	120.2	H18A—C18—H18B	109.5
C7—C6—H6A	120.2	O5—C18—H18C	109.5
C8—C7—C6	120.21 (10)	H18A—C18—H18C	109.5
C8—C7—H7A	119.9	H18B—C18—H18C	109.5
C6—C7—H7A	119.9	O7—C19—H19A	109.5
C9—C8—C7	119.10 (10)	O7—C19—H19B	109.5
C9—C8—H8A	120.4	H19A—C19—H19B	109.5

C7—C8—H8A	120.4	O7—C19—H19C	109.5
C8—C9—O2	116.45 (9)	H19A—C19—H19C	109.5
C8—C9—C10	122.36 (10)	H19B—C19—H19C	109.5
O2—C9—C10	121.14 (9)	O8—C20—H20A	109.5
C9—C10—C5	117.01 (9)	O8—C20—H20B	109.5
C9—C10—C17	120.20 (9)	H20A—C20—H20B	109.5
C5—C10—C17	122.79 (9)	O8—C20—H20C	109.5
N4—C11—N3	129.10 (10)	H20A—C20—H20C	109.5
N4—C11—O2	118.04 (9)	H20B—C20—H20C	109.5
C4—N1—C1—O3	178.40 (10)	C8—C9—C10—C17	179.84 (11)
C4—N1—C1—C2	-1.96 (15)	O2—C9—C10—C17	-2.78 (16)
C15—O3—C1—N1	1.42 (16)	C6—C5—C10—C9	0.94 (16)
C15—O3—C1—C2	-178.24 (11)	O1—C5—C10—C9	177.93 (10)
N1—C1—C2—C3	0.85 (16)	C6—C5—C10—C17	-179.62 (11)
O3—C1—C2—C3	-179.50 (10)	O1—C5—C10—C17	-2.62 (17)
N1—C1—C2—C11	-179.21 (8)	C14—N4—C11—N3	-1.47 (16)
O3—C1—C2—C11	0.44 (15)	C14—N4—C11—O2	177.68 (9)
C16—O4—C3—N2	-2.55 (15)	C12—N3—C11—N4	0.79 (16)
C16—O4—C3—C2	177.03 (10)	C12—N3—C11—O2	-178.39 (9)
C4—N2—C3—O4	178.15 (10)	C9—O2—C11—N4	-1.34 (13)
C4—N2—C3—C2	-1.42 (14)	C9—O2—C11—N3	177.94 (9)
C1—C2—C3—O4	-178.62 (10)	C19—O7—C12—N3	0.01 (14)
C11—C2—C3—O4	1.43 (14)	C19—O7—C12—C13	-179.72 (10)
C1—C2—C3—N2	0.95 (15)	C11—N3—C12—O7	-179.16 (9)
C11—C2—C3—N2	-178.99 (8)	C11—N3—C12—C13	0.55 (14)
C3—N2—C4—N1	0.15 (16)	O7—C12—C13—C14	178.67 (9)
C3—N2—C4—O1	179.26 (9)	N3—C12—C13—C14	-1.04 (15)
C1—N1—C4—N2	1.52 (16)	O7—C12—C13—C12	0.85 (14)
C1—N1—C4—O1	-177.62 (9)	N3—C12—C13—C12	-178.87 (8)
C5—O1—C4—N2	12.29 (13)	C20—O8—C14—N4	-9.19 (15)
C5—O1—C4—N1	-168.46 (9)	C20—O8—C14—C13	170.99 (11)
C4—O1—C5—C6	-121.76 (11)	C11—N4—C14—O8	-179.01 (10)
C4—O1—C5—C10	61.09 (13)	C11—N4—C14—C13	0.81 (14)
O1—C5—C6—C7	-177.67 (11)	C12—C13—C14—O8	-179.86 (10)
C10—C5—C6—C7	-0.51 (18)	C12—C13—C14—O8	-2.04 (14)
C5—C6—C7—C8	-0.20 (19)	C12—C13—C14—N4	0.31 (15)
C6—C7—C8—C9	0.43 (19)	C12—C13—C14—N4	178.14 (8)
C7—C8—C9—O2	-177.46 (11)	C18—O5—C17—O6	2.3 (2)
C7—C8—C9—C10	0.03 (18)	C18—O5—C17—C10	-177.92 (13)
C11—O2—C9—C8	-110.10 (11)	C9—C10—C17—O6	41.16 (17)
C11—O2—C9—C10	72.38 (13)	C5—C10—C17—O6	-138.26 (13)
C8—C9—C10—C5	-0.70 (16)	C9—C10—C17—O5	-138.63 (11)
O2—C9—C10—C5	176.68 (10)	C5—C10—C17—O5	41.94 (15)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C16—H16A $\cdots$ N1 <sup>i</sup>	0.96	2.58	3.5018 (19)	161

# supplementary materials

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C20—H20A $\cdots$ N3<sup>ii</sup>

0.96

2.59

3.5148 (19)

161

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $x, y+1, z$ .

Fig. 1

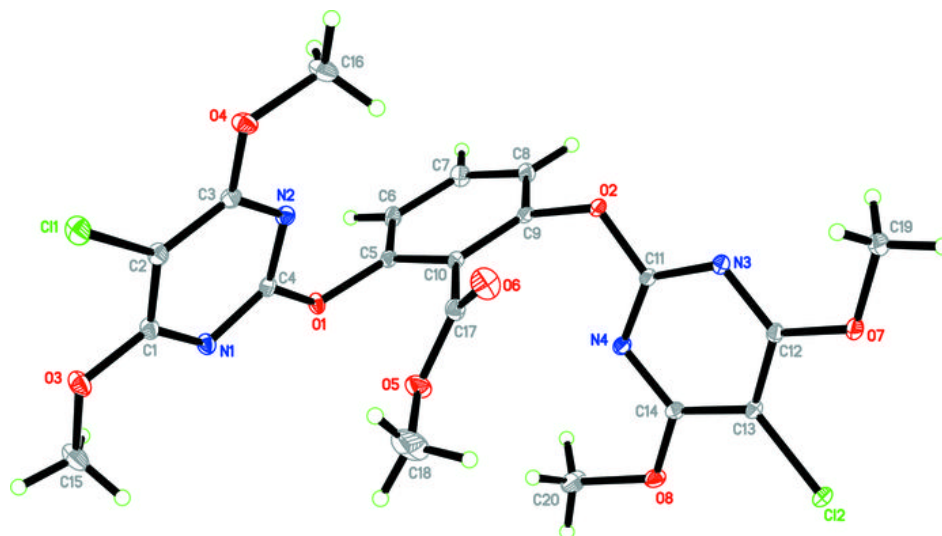


Fig. 2

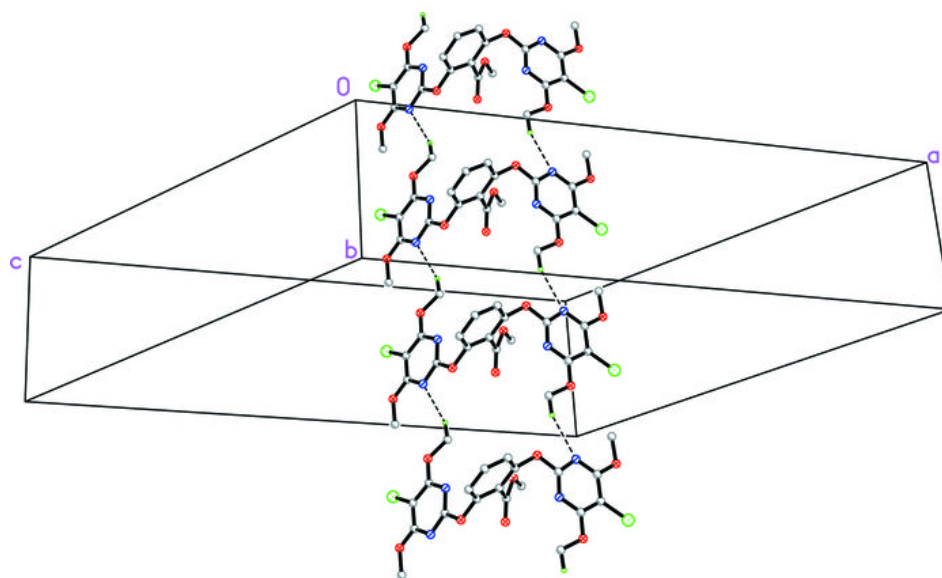


Fig. 3

